

SOLUTION PHASE REACTIONS OF ATOMIC HYDROGEN¹

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Key words: Hydrogen atoms, olefins, arenes, organosulfur compounds.

INTRODUCTION

We have recently developed a method for studying the reactions of hydrogen atoms in solution. The hydrogen atoms are generated in a flow system at 3 torr by a microwave discharge (2540-MHz) to produce a plasma of H₂ and He or H₂ alone (see Fig. 1).

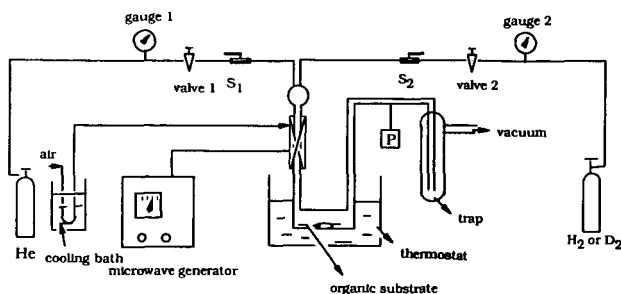


Fig. 1. Diagram of the Apparatus Used for the Generation of Atomic Hydrogen

The discharge gases are passed over a stirred solution of the substrate. Reactions take place and produce thermolyzed intermediates. The correlation of the products produced from these intermediates with the structure of the reactants yields fundamental and potentially useful information.

The reactions are efficient and surprisingly selective. Qualitatively the reaction rates follow the order:

disulfides > sulfides > olefins > aromatics > alkanes

Reactions with Olefins - Hydrogen or deuterium atoms produced from hydrogen or molecular deuterium in the cavity of a microwave generator were allowed to react with two olefins: 1-octene and 1-methylcyclohexene. A detailed mechanism for the formation of the products, both monomers and dimers, was determined. The addition reactions were regioselective, >99% addition to the terminal carbon of 1-octene and >99% to the secondary carbon of 1-methylcyclohexene. No products from allylic abstraction were detected. The product ratios for the addition of deuterium and protium were the same, see Tables 1 and 2.

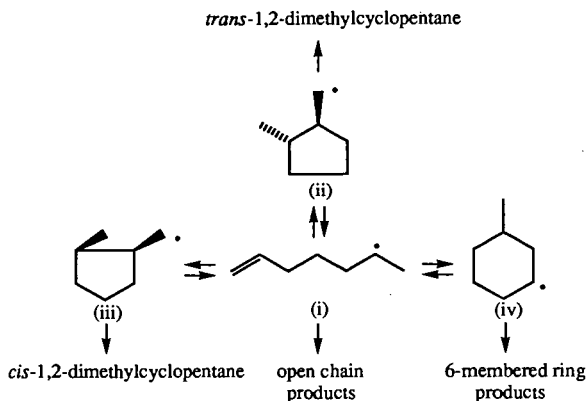
[Table 1 and 2]

The disproportionation to combination ratios (k_d/k_c) of the 1-methylheptyl and 1-methylcyclohexyl radicals were determined at several temperatures. The extrapolated ratios were found to be in good agreement with the literature values reported for reactions studied at room temperature.

The 1-methyl-5-hexenyl radical formed by the addition of a hydrogen atom to the terminal position of 1,6-heptadiene led to a complex mixture of products resulting from open chain and cyclized radicals, see Table 3.

[Table 3]

The cyclized radicals were formed reversibly and the final product mixture contained only minor amounts of *cis*-1,2-dimethylcyclopentane (the product of kinetic control) while the major cyclized product was methylcyclohexane. Although an equilibrium mixture could not be obtained the dimethylcyclopentyl and 3-methylcyclohexyl radicals were shown to be formed reversibly, see Scheme 1.



Scheme 1

Reactions with Sulfides and Disulfides - The reactions of hydrogen atoms with a series of unsymmetric disulfides were carried out. The regioselectivities and mechanisms of the reactions were investigated. The primary products of the reactions are thiol and thiyl radicals. The symmetric disulfides in the product mixtures were formed at -78°C by radical combination reactions, and not by radical displacements on the unsymmetric disulfides. The displacement, which favors attack of hydrogen on the least hindered sulfur is proposed to involve a metastable trivalent sulfur intermediate. The reactions of hydrogen atoms with a series of unsymmetric sulfides were carried out. A mechanism was proposed in which atomic hydrogen adds to the sulfur and forms an intermediate. The cleavage of the intermediate favors the most stable radical.

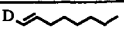
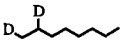
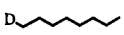
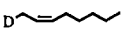
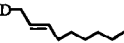
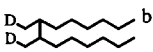
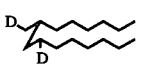
Reactions with Arenes² - When hydrogenation atom promoted sidechain fragmentation of arenes was investigated it was concluded that addition to the aromatic ring was reversible but that when ipso-attack occurs alkyl radical fragmentation may take place. Saturation of the ring is competitive with reversal or sidechain fragmentation. Polymerization of the arenes occurs even at 135°C . The model compounds studied were: toluene, bibenzyl, 9-dodecylantracene and dodecylbenzene.

ACKNOWLEDGMENT: We wish to thank the Natural Sciences and Engineering Research Council of Canada, the University of Alberta and the Department of Energy, Mines and Resources - CANMET for their generous support of the work.






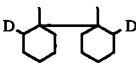
LITERATURE CITED

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2. Taken in part from the CANMET Final Report on "Low Temperature Hydrogenation of Bitumen Vacuum Residue and Syncrude Products Using Microwave Generated Hydrogen Free Radicals", 1993.

Table 1. The products, yields and mechanisms for the reaction of H• with 1-octene (-78°C)^a









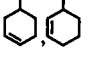
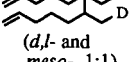
Products	Yield (%)	Mechanism ^c
	17.1	addition-disproportionation
	26.9	addition-addition
	30.8	addition-disproportionation
	2.8	addition-disproportionation
	9.1	addition-disproportionation
	11.8	addition-dimerization
	1.4	addition-radical addition

^a Neat 1-octene.^b A (1:1) mixture of *meso*- and *d,l*-dimers.^c Monodeuterated alkane/monodeuterated alkene = 1.^d $k_d/k_c = 2.4$ at -78°C.**Table 2.** The products, yields and mechanisms for the reaction of H• with 1-methylcyclohexene (-78°C)^{a,b}

Products	Yield (%)	Mechanism ^d
	15.3	addition-disproportionation
	7.9	addition-disproportionation
	20.2	addition-addition
	39.4	addition-disproportionation
	15.3	addition-disproportionation
	1.5	addition-dimerization
other ^c	0.5	addition-dimerization

^a Neat 1-methylcyclohexene.^b Monodeuterated alkane/monodeuterated alkene = 1.^c Five dimeric products.^d $k_d/k_c = 26.2$.

Table 3. Reaction of D• with 1,6-Heptadiene^{a,b}

	Product %	Proposed Mechanism ^c
	12.5	D atom addition - disproportionation
	26.3	D atom addition - disproportionation
	8.7	D atom addition - D atom addition
 (<i>trans</i> - + <i>cis</i> -)	11.4	D atom addition - disproportionation
	6.0	D atom addition - cyclization - D atom addition
	5.3	D atom addition - cyclization - disproportionation
	3.9	D atom addition - cyclization - disproportionation
	7.0	D atom addition - cyclization - D atom addition
	5.8	D atom addition - cyclization - disproportionation
 (<i>d,l</i> - and <i>meso</i> -, 1:1)	13.1	D atom addition - combination

^a Concentration in acetone (0.16 M).

^b Conversion = 3.1%.

^c P₆/P₅ = 1.46 (six membered ring/five membered ring products); monodeuterated alkane/monodeuterated alkene; k_d/k_c = 2.3 (-78°C).